

ELECTROCONDUCTIVE POLYAMIDE RESIN COMPOSITION AND MOLDED PRODUCT FOR MOTOR COMPONENT PREPARED THEREFROM

BACKGROUND OF THE INVENTION

Field of the Invention

5 The present invention pertains to a polyamide resin composition, and more specifically, to an electroconductive polyamide resin composition having high flowability, suitable for use in molding extrusion or injection components for motor vehicles requiring flexibility, impact resistance and conductivity, for example, a fuel filter housing, a fuel line, a fuel inlet tube, a fuel tank and the like
10 that deliver fuel to a motor vehicle engine.

Description of the Prior Art

 In general, polyamide resins are excellent in mechanical properties (e.g., tensile strength, flexible strength and elastic modulus), heat resistance and chemical resistance, and thus can be variously applied in the fields of all
15 industries including motor vehicles, or sports. Compositions having diverse functionalities have also been applicable to many components for motor vehicles. These days, in fuel system component materials for motors, plastics have been substituted for conventional metallic materials owing to their lightweight properties, low cost and no erosion in motors. Further, polyamide resin has
20 excellent resistance against gasoline and is employed to most fuel system components. Although a fuel filter housing or a fuel line in fuel system components should be resistant against gasoline, since they are in contact with gasoline all the time, such components have until now been made from metallic materials. Thus, polyamide resin having excellent gasoline resistance is suitable
25 for use in preparation of such motor parts.

 However, in the case of using polyamide lacking conductivity, a property

necessary for fuel system components such as a fuel filter housing and a fuel line, when gasoline is fed to the engine cylinder of motors at a very rapid rate, electrostatic charges are generated due to friction between the fuel and the walls of the fuel line, and are concentrated in any one portion. Such concentrated
5 electrical charges at any point of time are discharged at portions closest to adjacent metals. Continuous generation of such phenomenon results in fine cracks at discharged portions, through which gasoline is leaked, thus causing the danger of fire or explosion. Therefore, such motor components should have electroconductivity, capable of dissipating the static electricity to the vehicle body.

10 Additionally, the motor components should not be easily broken or cracked upon jarring or collision. In particular, when continuously driven in a cold area, the motor will suffer from such low temperature. So, high impact resistance and flexibility are required for the motor components.

In this regard, U.S. Pat. Nos. 5,164,084 and 5,164,879 disclose a 8 %
15 stainless steel fiber-containing polyamide-12 resin composition, which can be applied to a fuel filter housing component with conductivity, gasoline resistance and impact resistance while retaining volume resistivity of 10^6 Ohm-cm or less. But its preparation cost is very high and the composition is somewhat poor in flexibility and impact resistance. In U.S. Pat. Nos. 4,655,964 and 4,702,859, a
20 polyamide resin composition is difficult to apply to a fuel filter housing, a fuel line and a fuel inlet tube because of its low impact resistance, flexibility and moldability. Japanese Patent No. Sho 58-93756 refers to a composition for application to fuel system components of motor vehicles comprising polyamide resin, ethylene based elastic copolymer and carbon black, from which a molded
25 article is prepared, retaining electroconductivity and impact resistance but not providing high flexibility, impact and flowability. In addition, a composition comprising polyamide resin and 8-20 % by weight of metallic fiber and carbon fiber for molding fuel system parts of motor vehicles, disclosed in U.S. Pat. No.

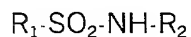
U.S. Pat. No. 4,655,964 refers to a conductive nylon composition comprising a linear nylon resin, 20-50 % by weight of mineral filler (kaolin, calcium metasilicate) and 4-6 % by weight of carbon black, with slight conductivity. But the nylon composition suffers from low impact resistance, flexibility and moldability. Also, in U.S. Pat. No. 4,702,859, a conductive polyamide resin composition comprising 100 parts by weight of xylenediamine and aliphatic dicarboxylic acid-derived polyamide, 5-100 parts by weight of polyamide-66 resin, 30-300 parts by weight of glass fiber, 5-40 parts by weight of carbon black and 5-40 parts by weight of graphite, is excellent in conductivity, mechanical strength, elastic modulus and heat deflection temperature, but very poor in impact resistance and flexibility. As well, preparation cost is high and thus financial loss occurs. EP 0 327 384 refers to a conductive polyacetal composition having improved flexibility and toughness, which meets electrical conductivity standards but suffers from impact resistance, flexibility and

resin composition.

DETAILED DESCRIPTION OF THE INVENTION

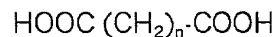
To achieve the above objects, the present invention provides an electroconductive resin composition comprising (a) 40-70 % by weight of semi-crystalline polyamide resin; (b) 15-40 % by weight of thermoplastic elastomer grafted with 0.5-2.0 % by weight of maleic anhydride; (c) 9-20 % by weight of carbon black powder; (d) 1-10 % by weight of sulfonamide based material, represented by the following formula 1; and (e) 0.001-0.02 % by weight of dicarboxyl based material, represented by the following formula 2.

Formula 1



(wherein, R_1 and R_2 are selected from the group consisting of alkyl, benzyl, phenyl, alkylphenyl and dialkylphenyl, wherein the alkyl is C_nH_{2n+1} ($n \leq 8$))

Formula 2



Further, the present invention provides an electroconductive resin composition characterized in that the polyamide resin has a relative viscosity of 2.8-3.5, and is selected from the group consisting of polyamide-6, polyamide-66, polyamide resin copolymers thereof, or mixtures thereof.

Also, the present invention provides an electroconductive resin composition characterized in that the conductive carbon black is selected from the group consisting of furnace black, Ketjen black, acetylene black and thermal black, and has a specific surface area (BET) of 500 m^2/g or more and an oil absorption (DBP) of 200 ml/100 g or more.

Additionally, the present invention provides an electroconductive resin composition characterized in that the sulfonamide based material is selected from the group consisting of N-propyl benzene sulfonamide, N-butyl benzene sulfonamide, N-hexyl benzene sulfonamide, N-octyl benzene sulfonamide, N-phenyl benzene sulfonamide, N-dimethylphenyl benzene sulfonamide, N-isopropylphenyl benzene sulfonamide, N-butylphenyl benzene sulfonamide, N-methyl methylbenzene sulfonamide, N-ethyl methylbenzene sulfonamide, N-butyl methylbenzene sulfonamide, N-butyl butylbenzene sulfonamide, N-butyl isopropylbenzene sulfonamide, N-butyl butylbenzene sulfonamide, N-phenyl methylbenzene sulfonamide, N-dimethylphenyl methylbenzene sulfonamide, N-isopropylphenyl methylbenzene sulfonamide, or mixtures thereof.

Further, the present invention provides an electroconductive resin composition characterized in that the thermoplastic elastomer is selected from the group consisting of polyethylene, polypropylene, polybutene, polyisoprene ethylene-propylene rubber, ethylene-propylene-diene rubber, ethylene-butene rubber, ethylene-octene rubber, ethylene-acryl rubber, styrene-ethylene-butylene-styrene copolymer, or mixtures thereof.

Furthermore, the present invention provides an electroconductive resin composition characterized in that the relative viscosity of the semi-crystalline polyamide resin is measured for a solution of 1 g of resin in 100 ml of 96 % sulfuric acid with Ubbelohde viscometer.

In addition, the present invention provides a molded product for motor vehicle components prepared from the electroconductive resin composition.

Furthermore, the present invention provides a molded product characterized in that the motor components are a fuel filter housing or a fuel line.

Hereinafter, a detailed description will be given of the present invention.

dissolved in gasoline. At high grafted ratios of maleic anhydride, dispersability is increased and dissolution in gasoline becomes low, but flowability is decreased. Hence, it is preferred that maleic anhydride is used in the amount of about 2.0 % by weight. Such thermoplastic elastomer may be appropriately used according to diverse applications, and in general, use of about 15-40 % by weight of the elastomer leads to drastically increased impact resistance.

Examples of useful thermoplastic elastomers include polyethylene, polypropylene, polybutene, polyisoprene ethylene-propylene rubber, ethylene-propylene-diene rubber, ethylene-butene rubber, ethylene-octene rubber, ethylene-acryl rubber and styrene-ethylene-butylene-styrene copolymer.

As carbon black usable to render the composition electrically conductive, furnace black, Ketjen black, acetylene black and thermal black can be used. Of them, Ketjen black is the most preferable.

Additionally, it is preferred that carbon black has specific surface area (BET) of 500 m²/g or more and oil absorption (DBT) of 200 ml/100 g or more (Plastics Engineering/April '95, pp. 29-32; "Special Carbon Blacks for Plastics").

Although the conductive carbon black is used in different amounts according to its type, it ranges from 9 to 20 % by weight, preferably. If possible, to obtain the objective electroconductivity by using small amounts of carbon black, processing conditions and combinations of material components should be optimized. When the amount of carbon black is less than 9 % by weight, conductivity becomes poor. Whereas, when the amount exceeds 20 % by weight, flowability, impact resistance and flexibility are drastically decreased. So, it is favorable that the conductivity is maximized by use of 20 % by weight or less of carbon black.

The sulfonamide based material used to make the composition flexible

As the representative sulfonamide based materials, use can be made of any one comprising N-propyl benzene sulfonamide, N-butyl benzene sulfonamide, N-hexyl benzene sulfonamide, N-octyl benzene sulfonamide, N-phenyl benzene sulfonamide, N-dimethylphenyl benzene sulfonamide, N-isopropylphenyl benzene sulfonamide, N-butylphenyl benzene sulfonamide, N-methyl methylbenzene sulfonamide, N-ethyl methylbenzene sulfonamide, N-butyl methylbenzene sulfonamide, N-butyl butylbenzene sulfonamide, N-butyl isopropylbenzene sulfonamide, N-butyl butylbenzene sulfonamide, N-phenyl methylbenzene sulfonamide, N-dimethylphenyl methylbenzene sulfonamide, and N-isopropylphenyl methylbenzene sulfonamide. Most preferably, N-butyl benzene sulfonamide is used. The composition prepared from the above components can be applied to various molded products, because of its good physical properties, namely, impact resistance, conductivity, flexibility and so on. In practice, rapid molding is performed to reduce preparation costs and to increase productivity. To meet such conditions, the composition itself should have high flowability favorable in terms of molding. With a view to realize the above goals, it is found that use of 0.001-0.02 % by weight of dicarboxyl based material (formula 2) results in drastically increased flowability while maintaining all properties. If the amount is less than 0.1 % by weight, flowability is minimally improved, whereas if the amount exceeds 0.3 % by weight, workability in the extruder becomes lowered.

In addition, processing stabilizers, lubricants, antioxidants, brighteners, dispersants, nucleating agents may be added to obtain various effects, within the scope of the present invention.

Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

EXAMPLES 1-7

(a) polyamide-6 resin or polyamide-66 resin having relative viscosity (measured for a solution of 1 g of sample in 100 ml of 96 % sulfuric acid with Ubbelohde viscometer) of 3.0, (b) Ketjen black as a conductive carbon black, (c) N-butyl benzene sulfonamide as a softner, (d) thermoplastic elastomer and (e) dicarboxyl based material, were mixed at the ratios shown in the following table 1, using a single screw or a twin screw extruder. In these examples, a twin screw extruder having L/D of 30, supplied from Toshiba Corporation, was used. As such, the processing temperature was 240-280 °C and screw rotation rate was 200-300 rpm. The lace obtained through a nozzle from the mixed composition was cooled with water in a cooling bath, pelletized using a cutter, and then dried at 95 °C in a drier under nitrogen atmosphere for 5 hours, to prepare test pieces, which were then measured for various properties. The results are shown in Table 3, below.

COMPARATIVE EXAMPLES 1-5

In order to investigate the effect of compositions out of the range of the present invention, the compositions according to mixing ratios of the table 2 were prepared, and measured for their properties. The results are presented in Table 4, below.

TABLE 1

(unit:wt%)

Composition	Example No.						
	1	2	3	4	5	6	7
Polyamide-6 resin (#1)	65.8	67.8	58.5		49.5	49.8	45.8
Polyamide-66 resin (#2)				52.5			
Thermoplastic Elastomer(#3)	20	15	25	30	30	35	35
Carbon Black(#4)	9	10	11	12	15	12	12
Sulfonamide based Material(#5)	5	5	5	5	5	3	7
Dicarboxyl based Material(#6)	0.2	0.2	0.5	0.5	0.5	0.2	0.2

- #1: pellet type polyamide-6 resin having relative viscosity of 3.0 measured for a solution of 1 g of resin in 100 ml of 96 % sulfuric acid with Ubbelohde viscometer
- #2: pellet type polyamide-66 resin having relative viscosity of 2.8 measured for a solution of 1 g of resin in 100 ml of 96 % sulfuric acid with Ubbelohde viscometer
- #3: Kraton FG 1901X, supplied from Shell Chemical
- #4: Vulcan XC-72, supplied from Cabot Corporation
- #5: N-butyl benzene sulfonamide
- #6: $\text{HOOC}-(\text{CH}_2)_{10}-\text{COOH}$

TABLE 2

(unit:wt%)

Composition	Comparative Example No.					
	1	2	3	4	5	6
Polyamide-6 resin (#1)	64.5	63.5		53.8	52.8	
Polyamide-66 resin (#2)			53.0			44.5
Thermoplastic Elastomer(#3)	30	10	30	35	35	35
Carbon Black(#4)	15	11	12	8	12	12
Sulfonamide based Material(#5)		5	5	3		7

Dicarboxyl based Material(#6)	0.5	0.5		0.2		1.5
<p>#1: pellet type polyamide-6 resin having relative viscosity of 3.0 measured for a solution of 1 g of resin in 100 ml of 96 % sulfuric acid with Ubbelohde viscometer</p> <p>#2: pellet type polyamide-66 resin having relative viscosity of 2.8 measured for a solution of 1 g of resin in 100 ml of 96 % sulfuric acid with Ubbelohde viscometer</p> <p>#3: Kraton FG 1901X, supplied from Shell Chemical</p> <p>#4: Vulcan XC-72, supplied from Cabot Corporation</p> <p>#5: N-butyl benzene sulfonamide</p> <p>#6: HOOC-(CH₂)₁₀-COOH</p>						

TABLE 3

Measurement of Properties (Examples)

(unit:wt%)

Properties	Example No.						
	1	2	3	4	5	6	7
Volume Resistivity, log(Rv)(Ω) #1	65.8	67.8	58.5		49.5	49.8	45.8
Flexible Elastic Modulus (Mpa) #2				52.5			

Tensile Fracture Elongation (%) #3	20	15	25	30	30	35	35
Izod Impact Strength (kg.cm/cm) #4	9	10	11	12	15	12	12
Melt Index (MI) #5	5	5	5	5	5	3	7
<p>#1: volume resistivity, measured with 40x40x3mm square test piece using Ultra Megohmmeter (Japan TOA Co.) at 500 volt, 60 sec according to ASTM D-257, and shown as log value</p> <p>#2: measured with flexible strength piece according to ASTM D-790, the smaller the value, the more flexible the product</p> <p>#3: measured with tensile strength piece according to ASTM D-638</p> <p>#4: measured according to ASTM D-256, at notched state</p> <p>#5: measured at 275°C under 2.16 kg load according to ASTM D-1238, at larger values, flowability is increased and thus moldability becomes more favorable</p>							

TABLE 4

Measurement of Properties (Comparative Examples)

(unit:wt%)

Properties	C. Example No.				
	1	2	3	4	5

Volume Resistivity, log(Rv)(Ω) #1	3	6	4	11	6
Flexible Elastic Modulus (Mpa) #2	2000	2800	1000	700	1500
Tensile Fracture Elongation (%) #3	12	10	40	110	25
Izod Impact Strength (kg.cm/cm) #4	10	5	50	88	70
Melt Index (MI) #5	9	12	1	7	0.3
<p>#1: volume resistivity, measured with 40x40x3mm square test piece using Ultra Megohmmeter (Japan TOA Co.) at 500 volt, 60 sec according to ASTM D-257, and shown as log value</p> <p>#2: measured with flexible strength piece according to ASTM D-790, the smaller the value, the more flexible the product</p> <p>#3: measured with tensile strength piece according to ASTM D-638</p> <p>#4: measured according to ASTM D-256, at notched state</p> <p>#5: measured at 275 °C under 2.16 kg load according to ASTM D-1238, at larger values, flowability is increased and thus moldability becomes more favorable</p>					

As described above, the electroconductive resin composition of the present invention has a volume resistivity of 10^5 (log value=5)Ω cm or less and has excellent impact resistance. As well, the composition has the advantages of high flexibility and flowability, and superior moldability, thereby being applicable to electroconductive extrusion and injection components, in particular, fuel system components for motor vehicles.

The present invention has been described in an illustrative manner, and it

is to be understood that the terminology used is intended to be in the nature of description rather than of limitation. Many modifications and variations of the present invention are possible in light of the above teachings. Therefore, it is to be understood that within the scope of the appended claims, the invention may

5 be practiced otherwise than as specifically described.